Characterization of Coupled Hydrologic-Biogeochemical Processes Using Geophysical Data

1. Research Objectives:

Biogeochemical and hydrological processes are naturally coupled and variable over a wide range of spatial and temporal scales. Many remediation approaches also induce *dynamic* transformations in natural systems, such as the generation of gasses, precipitates and biofilms. These dynamic transformations are often coupled and can reduce the hydraulic conductivity of the geologic materials, making it difficult to introduce amendments or to perform targeted remediation. Because it is difficult to predict these transformations, our ability to develop effective and sustainable remediation conditions at contaminated sites is often limited. Further complicating the problem is the inability to collect the necessary measurements at a high enough spatial resolution yet over a large enough volume for understanding field-scale transformations.

Our research focuses on investigating the capability to characterize and monitor complex transformations that occur during remediation at appropriate resolutions and spatial scales using geophysical data. In particular, we are investigating the influence of evolved gasses, precipitates, and biofilms on geophysical signatures using seismic, radar, and electrical techniques. We have performed several controlled column scale experiments as well as a field scale experiment to explore the potential of minimally invasive geophysical methods for monitoring system transformations during remediation.

2. Research Progress and Implications:

In this section, we review the research project progress in the third year of a three-year project. Our research has focused on investigating the utility of time-lapse geophysical methods to detect biogeochemical-hydrological (BGH) transformations that occur during remediation at both the laboratory and the field scales.

Investigations at the Laboratory-Scale.

We have investigated the capability of time-lapse geophysical methods (seismic, radar, SP and complex electrical) for remotely detecting changes in BGH properties as a system is perturbed. Using column-scale experiments, we have tested the sensitivity of the different geophysical methods to reaction products that occur during biostimulation, such as gasses, precipitates, and biofilms. The experimental columns were instrumented along their length with geophysical sensors, as well as with biogeochemical fluid sampling ports. As an example of our research in this area, we have examined microbe-induced ZnS and FeS precipitation during a biostimulation experiment performed using *Desulfivibrio vulgaris* (a sulfate-reducing bacterium that couples the incomplete oxidation of lactate to acetate with sulfate reduction). Several pore volumes of lactate were flushed through the system before the experiment started, at which time bacteria were introduced into the middle of the column and the nutrients were introduced into the bottom of the upward-flowing column. Geophysical, hydrological, and biogeochemical measurements were collected using an experimental suite of columns. Sulfate reduction was monitored over seven weeks, and was indicated by decreasing substrate and metals concentrations, increasing biomass, and visually discernable regions of metal sulfide accumulation. The region of sulfide precipitation showed a shift toward the influent portion of the column over time as a result of microbial chemotaxis towards elevated substrate concentrations at the base of the column. Regions of sulfide precipitation and accumulation resulted in substantial changes in seismic and complex electrical measurements. High-frequency seismic wave amplitudes were reduced by nearly 84%, as is illustrated in Figure 1 (Williams et al., 2005). The largest overall decreases in amplitude occurred in the regions nearest the base of the column, and hence closest to point of substrate influx. The decreased acoustic wave amplitudes may be explained by using a patchy saturation model, wherein wave-induced flow results from the heterogeneous formation of high bulk modulus sulfide precipitates within formerly fluid-filled pores. Significant increases in complex electrical conductivity measurements (Figure 2) were observed with only minimal changes in the fluid conductivity over the frequency range recorded (0.1–1000Hz).

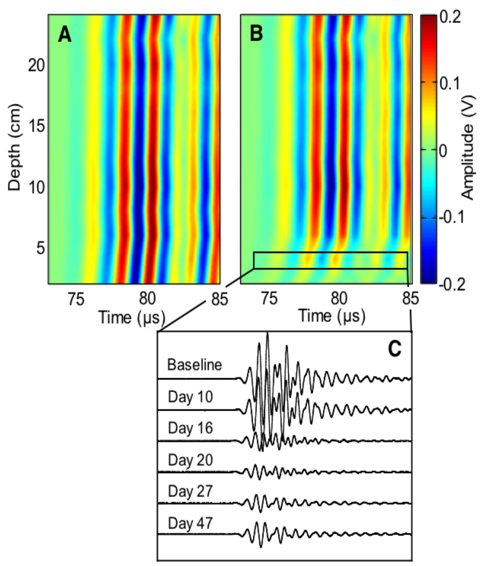

Figure 1 Changes in seismic waveforms near base of column as a function of time after inoculation.

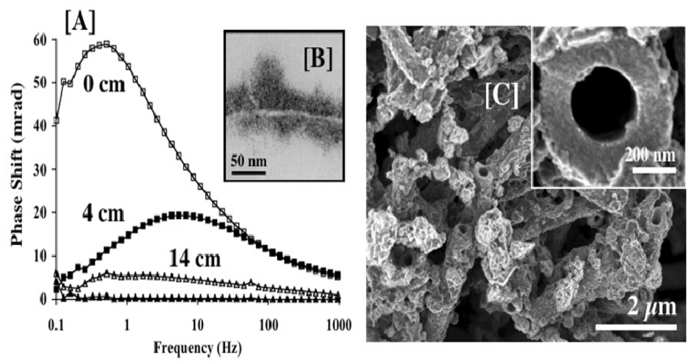

Figure 2 [A] Maximum phase shift relative to baseline for four locations along the length of the column; [B] Cross sectional TEM image of a single *Desulfovibrio vulgaris* cell with membrane-bound ZnS and FeS precipitates. [C] SEM image of metal sulfide encrusted microbes and spherical aggregates; high-resolution SEM image of a fractured cell encrusted in compositionally mixed ZnS and FeS [inset]. Both [B] and [C] represent samples recovered from the 0 cm location in [A], which is nearest to the column inlet. These images and provide direct evidence of the products of biomineralization and their impact of complex resistivity signatures (Williams et al., 2005).

Changes in the IP response are attributed to alterations in subsurface mineralogy arising from stimulated microbial activity within the pore space, including precipitation reactions, aggregation dynamics, and solid-state mineral transformations (Williams et al., 2005; Ntarlagiannis et al., 2005). This experiment suggested that geophysical techniques are capable of detecting the onset and evolution of microbe-induced sulfide precipitation, and that frequency-dependent electrical measurements are sensitive to pore-space alterations in mineralogy, including precipitation of insoluble phases, mineral aggregation dynamics, and solid-state transformations of aqueous contaminants sequestered as solids (e.g. uranium, strontium, chromium, and heavy metals).

We have additionally conducted several other laboratory batch or column experiments to investigate the sensitivity of different geophysical methods to changes that occur during remediation. The results of these studies are briefly described below.

- *Radar measurements to detect onset and evolution of gas during denitrification.* Radar velocity measurements were used with a mixing model to estimate the volume of originally water saturated pore space that was replaced by N_2 gas over time during a biostimulation experiment developed to encourage denitrification. The radar information detected gas volumes as low as 5% and estimated a final gas saturation over the entire column of 24.6%, which compared favorably with the effective gas saturation value estimated using column weight loss measurements of 23.3% (Hubbard and Williams, 2004). This experiment suggested that the radar measurements are sensitive to the onset and extent of gaseous end products of denitrification, and by extrapolation, methanogenesis.

- *Seismic measurements to detect onset of gas evolution during denitrification.* We investigated the sensitivities of seismic amplitude and velocity to gas generation during a biostimulation experiment, where *Pseudomonas stutzeri* was used with nitrate as the electron acceptor. We found that seismic amplitudes were very sensitive to gas generation, and that small quantities of evolved gasses greatly diminished the seismic amplitude to sometimes non-detect levels. This suggests that seismic amplitudes are a good indicator for *early onset* of denitrification.
- *SP measurements for characterization of redox conditions.* We have used the self-potential (SP) method to track the onset and location of microbial sulfate-reduction in saturated sediments at the laboratory scale during conditions of organic carbon amendment. Anomalies of greater than –400 mV were observed as sulfate-reduction coincided with the incomplete oxidation of lactate. The timing and location of the SP anomalies correlated with increases in the concentration of planktonic cells and decreases in sulfate, and are believed to result from electrochemical concentration gradients between regions of high and low dissolved sulfide. Temporal variations in the location of the SP anomaly corresponded to the location of active sulfate-reduction, which in turn was governed by microbial chemotaxis towards elevated lactate concentrations. Abiotic experiments in which sulfide concentration gradients were systematically varied showed a positive correlation between the magnitude of the measured SP anomaly and the difference in sulfide concentration. These results suggest the ability to measure the changes in the spatiotemporal location of sulfate-reduction during bioremediation and to perhaps quantify the ensuing sulfide concentration gradients (Williams et al., 2005b).
- *IP methods to track changes in iron mineralogy during remediation.* Under conditions of biostimulation, consumption of such accessible ferric compounds by iron-reducing microorganisms can result in elevated rates of respiration and successful contaminant remediation. As these compounds are exhausted and more recalcitrant forms of ferric iron are accessed, competition by other microbial strains, such as sulfate-reducers, can result in metabolic processes less favorable to sustained remediation efficacy. We have used IP methods to track physiochemical changes in iron-bearing clays resulting from microbial respiration, which correlated with the exhaustion of bioavailable ferric compounds (Williams et al., 2005c). This study suggests that IP methods may be a reasonable approach for noninvasively monitoring the sustainability of prolonged iron-reduction under stimulated conditions.
- *Combined seismic and IP methods to monitor biomass accumulation.* We investigated the use of seismic and IP methods to characterize the accumulation of biomass within saturated sediments. The experimental conditions were similar to those used during our studies of metal sulfide precipitation, with the exception that no metals were added to the influent solution. Although destructive evaluation of the sediments revealed significant biofilm development, only modest changes in IP and seismic signatures were observed (Ntarlagiannis et al., 2005).

Investigations at the Field Scale

We have also tested the use of geophysical methods for elucidating system transformations at the field scale during remediation. With EMSP support, we have used geophysical methods to detect system transformations associated with an ongoing NABIR project (performed by Phil Long of PNNL, Derek Lovely of UMass, and a multi-investigator NABIR team) being conducted at the Rifle, Colorado UMTRA Site. At this site, we monitored a biostimulation experiment aimed at reducing elevated concentrations of uranium in a shallow aquifer using surface-based complex resistivity data. Figure 3 shows the phase changes associated with 0.125 Hz complex resistivity data collected near the stimulation wells (I) at the Rifle site three and ten weeks after stimulation was initiated. We interpret the changes to be associated with the reduction of iron-containing minerals within the bioavailable clay-sized fraction of the sediments, which decreases the mineral surface area and thus the polarizability. Our results suggest that variations in complex resistivity are indicative of the effective changes in mineral transformations associated with microbial iron-reduction, which are related to decreases in uranium concentrations and changes in aquifer redox conditions. Because sustainability of low U(VI) concentrations at this site is governed by redox conditions favorable to iron-reduction, such surface-based imaging could be extremely useful for understanding system transformations *over distances of tens to hundreds of meters.*

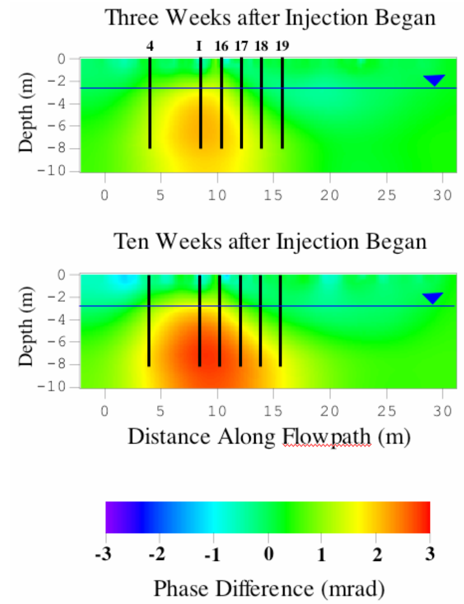

Figure 3 Change in phase response of aquifer sediments at the "field scale" that is interpreted to be a result of alterations in iron mineralogy brought about through biostimulation.

3. **Planned Activities**

Collectively, our lab and field-scale tests suggest that minimally invasive, high-resolution geophysical methods hold significant potential for monitoring and elucidating processes that occur during remediation over a variety of spatial scales. These results suggest a novel approach for remotely investigating complex biogeochemical phenomena, and for monitoring metal-contaminated aquifers undergoing bioremediation to ensure the effectiveness and stability of the treatment. Our laboratory scale experiments have been performed under fairly ideal conditions (i.e., systems poised to undergo single process), and the field scale imaging has been used to indicate (rather than to estimate) the processes that occurred during stimulation. The methods developed by Chen et al. (2004) could be modified to be used to estimate system transformations using geophysical data. Additionally, more research is needed to enable quantitative use of the remote methods under naturally heterogeneous conditions and in the presence of multiple "processes" (i.e., the development of gasses, biofilms, and precipitates). Although this is the last year of our project, our research suggests that further investigation is warranted, and we are applying through EMSP to expand the exploration of the utility of geophysical data for remote monitoring of system transformations.

4. Information Access:

This project has additionally been the focus of several publications and presentations at professional conferences. In particular, the study published in ES&T was highlighted in their A-Pages: http://pubs.acs.org/subscribe/journals/esthag-w/2005/aug/tech/rp_microbes.html. The references for these papers are given below, many of which are available for download at: http://esd.lbl.gov/people/shubbard/vita/webpage/monitoring.html

<u>Accepted or Published Manuscripts:</u>

1. Chen, J, S. Hubbard, E. Rodin, C. Murray and E. Majer, Estimation of geochemical parameters using geophysical data, *Water Resources Research,* v. 40, W12412, doi: 1029/2003WR002883, 2004.
2. Kenneth H. Williams, Dimitrios Ntarlagiannis, Lee D. Slater, Alice Dohnalkova, Susan S. Hubbard, and Jillian F. Banfield, Geophysical Imaging of Stimulated Microbial Biomineralization *Environ. Sci. Technol*.; DOI: 10.1021/es0504035, Aug 2005.
3. Ntarlagiannis’ D., K. H. Williams, L. Slater and S. Hubbard, IP response of microbial induced sulfide precipitation, accepted for publication in *Journal of Geophysical Research*, 2005.

<u>Manuscripts in Submission/Development</u>

1. Monitoring Microbial Chemotaxis and Sulfate-Reduction Using the Self-Potential Method
2. Geophysical Monitoring of the In Situ Activity of *Geobacter* Species

<u>Abstracts / Presentations:</u>

1. Hubbard, S., J. Chen, K. Williams, J. Peterso^{n}, and Y. Rubin’ Environmental and Agricultural Applications of GPR, IWAGPR 2005 Keynote speaker, Delft Netherlands May 2-4, 2005.
2. P. Long, D. Lovley, K. Nevin, R. O’Neil, C. T. Resch, A. Peacock, H. Vrionis, D.Holmes, Y. Chang, R. Dayvault, I. Ortiz-Bernad, K. Williams, S. Hubbard, S. Yabusaki, Y. Fang, R. T. Anderson, and D. C. White, Field-scale Biostimulation of U(VI) Reduction in a Shallow Alluvial Aquifer, ISSM Meeting, Jackson Hole, WY, 2005.
3. Williams, K., S. Hubbard, and J. Banfield, Monitoring microbial chemotaxis and sulfate reduction using the self-potential method, *Eos Trans. AGU,* 86(18), Jt. Assem. Suppl., Abstract NS51B-07, 2005b.
4. K. H. Williams, P. E. Long, E. Shelobolina, S. S. Hubbard, and J. F. Banfield, Non-Invasive Geophysical Monitoring of Microbe-Mediated Clay-Mineral Transformations, ISSM meeting, Jackson Hole, WY, 2005c.
5. K. H. Williams, D. Ntarlagiannis, P. Long, A. Dohnalkova, S. S. Hubbard and J. F. Banfield , 2004 Invited talk, Remote Sensing of Subsurface Microbial Transformations, Eos Trans. AGU, 85(47), Fall Meet. Suppl., B51F-01, 2004.